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New Routes to Recycle Scrap Tyres

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1. Introduction

Most means of transport need tyres as an essential component to work. Tyre composition is complex and is designed according to high technical standard requirements of adhesion, flexibility, forces and pressures, which are necessary for their functioning. However, tyres suffer from wear and have a limited lifetime due to its use. After their replacement, the unusable tyres are known as End of Life (EOL) tyres.

The crosslinked chemical structure of the rubber, the high amount of stabilizers and other additives present in tyres formulations make them a non-biodegradable, non-environmentally friendly material. The growing environmental awareness linked to the development of new european and national regulations have instigated the research for recovering EOL tyres for other applications.

A common industrial procedure prior to any form of recovery consists in grinding the tyre, in order to obtain a powder called ground tyre rubber (GTR). This powder has been proposed as a suitable reinforcement for composite materials as a way to reduce the amount of EOL tyres in added value applications. However, one of the main issues of working with GTR is its low compatibility with most of polymeric matrices used, mainly due to highly crosslinked rubber structure. Another drawback is related with the high particle size of GTR obtained by standard industrial grinding process (between 400 and 600 μm approximately) that results in brittle composite materials. Different methods have been already tested to compatibilize the polymer blends and to reduce GTR's particle size, turning out to be too expensive procedures to provide an economically competitive material.

In this chapter, several ways to blend GTR with commodity polymers were discussed. The proposed alternatives are based on the preparation of new composite materials using GTR as a reinforcement, thereby providing another way of adding value and reducing the stock of used tyres.

For the development of the proposed GTR based composites, it will be necessary to improve adhesion between matrix and rubber reinforcement. In this regard, the following methods have been carried out, which was discussed in this chapter: 1) acid pre-treatment of GTR materials, 2) use of wetting additives and waxes into the mixture and 3) use of a ternary blend to prepare a thermoplastic elastomer.

The effect of each proposed method on the mechanical and morphological properties of the GTR based composites was studied. Also, microstructural and chemical characterization of the composites was provided. Moreover, the materials have been optimized in order to

obtain composites reinforced with the highest GTR amount by keeping the most appropriated mechanical properties, an adequate processability and minimum cost.

In particular, the aforementioned methods proposed for the development of the GTR based composites will cover the following aspects:

1. A treatment with H_2SO_4 which improves the rubber's ability to interact with high density polyethylene matrix (HDPE). This treatment provides a greater stiffness to the GTR reinforcement, which is a consequence of rubber rigidification after the acidic treatment due to the extraction of additives and degradation;
2. Treatments with wetting additives and waxes which produce an increase in the mechanical properties of the polymer matrix (i.e. Young's modulus and tensile strength).
3. The use of ethylene propylene diene monomer rubber (EPDM) and peroxides as a third component for the production of thermoplastic elastomers materials based on reused tyres. A material containing up to 30% by weight (w/w) of GTR can be obtained by this method, which shows a combination of strength, toughness and elongation appropriate for industrial use.

2. Approach

Composites made out of ground tyre rubber and other polymers would have good adhesion if the ground tyre rubber would have pores, holes, crevices or other irregularities, unfortunately they do not. Ground rubber obtained by the cryogenic and room temperature methods are quite different.

Figure 1 shows that the major difference between particles of rubber generated by room temperature and cryogenic processing systems is their shape. Particles derived from the cryogenic process have a smooth surface, akin to shattered glass while the particles derived from the room temperature process have a rough surface, giving it greater surface area relative to the cryogenically produced particle [Adhikari 2000]. In later sections, it will be seen how the multilobed morphology of ambient GTR is not enough for an acceptable mechanical adhesion.

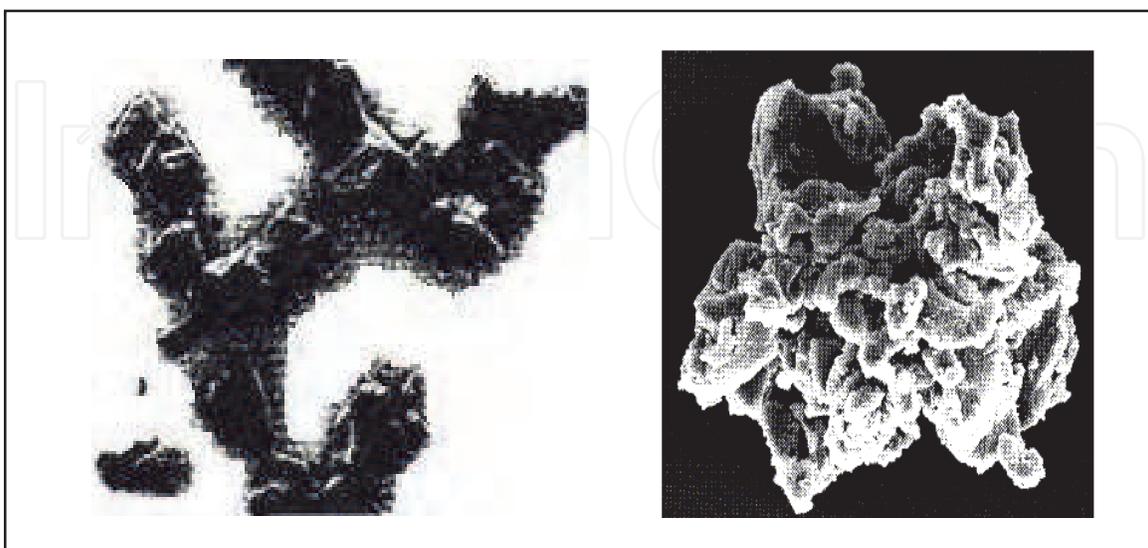


Fig. 1. Cryogenic ground rubber [Burford 1982] (x100 - left) and room temperature GTR [Erickson Materials] (x325 right).

2.1 Previous studies of composites based on GTR and thermoplastic matrices

Composites based on GTR and thermoplastics have not been deeply studied. Even so, some interesting and successful studies can be found in the literature.

Shojaei et. al. [Shojaei 2007] studied the behaviour of HDPE after degradation by re-extrusion. In order to improve the HDPE modulus and tensile strength, Polypropylene (PP) filled with 30 wt % of glass fiber was added. In addition, they studied the effect of GTR particles in the final product where they observed a lower stiffness due to its role (in that specific composite) as soft filler and an undesirable slightly increase in elongation. Unfortunately, ground tyre rubber did not produce any improvement on impact properties probably because of the low interfacial adhesion between the matrix and GTR particles. They finally concluded that the addition of ground tyre rubber particles into the final composition should be kept at low amounts (less than 10%wt).

Oliphant and Baker [Oliphant 1993] precoated the cryogenic GTR (CGTR) with ethylene acid acrylic copolymer and mixed it afterwards with LLDPE and HDPE matrixes. They found that the deleterious effects of the mixture could be overcome while still retaining composite processability. For example, a blend with 40 wt % of ethylene acid acrylic (EAA) coated CGTR particles with LLDPE had an impact and tensile strengths of 90% compared with those of pure LLDPE. However, very poor mechanical properties of the CGTR/HDPE composites were found with HDPE composites. This was believed to be because particles were too large to induce a brittle to ductile transition. The failure occurred largely through crack propagation and the large CGTR particles (even with moderate adhesion), acted as serious flaws, providing an easy path for the crack to follow. They concluded that the addition of CGTR to a semi-brittle matrix such as HDPE, requires much higher levels of adhesion (to retard the crack growth at the particle/matrix interface) or much lower particle sizes.

Another way to modify adhesion between these two incompatible phases is via radiation. Sonnier et. al. [Sonnier 2006] studied the influence of γ radiation on GTR/rHDPE (recycled) composites. Gamma irradiation allows achieving in situ compatibilisation, leading to an improvement of the mechanical properties. With irradiation doses of 25-50kGy the elongation at break and Charpy impact strength significantly increased. Only Young's modulus slightly decreased due to the fact that radiation induced also crosslinking of the rHDPE matrix.

The grafting of compatibilizers on GTR surface is another method to improve compatibility. Fuhrmann and Karger-Kocsis [Fuhrmann 1999] functionalized GTR with methacrylic acid and glycidyl methacrylate by photoinitiated polymerization. The process consists in UV radiation of GTR in presence of air and afterwards a process of grafting compatibilization is carried out. The presence of reactive carboxy and epoxy groups was demonstrated. The idea behind these studies is the creation of polar functional groups on the GTR surface that should result in increased reactivity and improved interfacial adhesion between the GTR and matrix polymers. Kim et. al. [Kim 2000] studied the mixture of HDPE filled with surface modified GTR particles round tyre rubber particles surface modified with acrylamide (AAm) using UV radiation. Ground tyre rubber particles and HDPE were extruded using a single-screw extruder and maleic anhydride-grafted polypropylene was added as a compatibilizer to improve adhesion between phases. They demonstrate an improvement in tensile stress, strain and impact strength.

2.2 Materials and general process for samples preparation

The basic materials used in this study were HDPE and GTR. Properties of those materials are described below. Other specific materials used in the different purposed methods will be described in the corresponding section.

The high density polyethylene (HDPE) used as matrix was supplied by REPSOL-YPF (ALCUDIA® 4810-B), with a density of 960Kg/m³. The HDPE was characterized by melt flow index (MFI_{190/2.16}) of 1.0g/10min, Young's modulus of 927.90MPa, tensile strength of 17.17MPa, elongation at break of 390.80% and toughness of 38.4J.

Two different suppliers provided the GTR particles: Gestión Medioambiental de Neumáticos S.L. (GMN) in Maials (Lleida, Spain) and Alfredo Mesalles (Barcelona, Spain), both with a average particle size between 0.4 and 0.6mm.

The mixing process for the composites was carried out in a two roll mill heated at 150-155°C. The HDPE matrix is melted for a minute and then, the GTR particles are added and mixed for another 5 minutes.

Composite sheets (150x150x2mm³) were prepared by hot press moulding at 100kN and 170°C for 10 minutes. After that step, the sample sheets are cooled for 5 minutes under pressure using - water. After that, the materials were mechanically shaped as test specimens according to ASTM-D-412-98 specifications.

2.3 Oxidant treatments on GTR surface in order to improve composites compatibility

Sulphuric and nitric acids have been used previously to modify GTR surface from tyre wastes resulting in a great porosity development [Manchón 2004][Sonnier2006]. According to these previous results the chemical attack produced by the acid on surfaces creates an appropriate morphology to improve interlocking between matrix and the GTR particles. On the other hand, it is worth to mention that acid treatments seem a financially worthwhile way to achieve a suitable material, due to the fact that their application does not require any specific equipment or complex technical processes.

These results lead to consider the possibility of using the main features of the pre-treated oxidised rubber to improve the mechanical adhesion of GTR/HDPE composites. The first method to improve adhesion between HDPE and ground tyre rubber consists on using three chemical acids, such as H₂SO₄, HNO₃ and a sulphuric-nitric solution (50/50% v/v), as GTR surface modifiers. The effect of the chemical and physical modifications on the GTR particles surface and the effect of this modification on the composites performance were monitored by determining its mechanical and structural properties, by the use of FTIR-ATR spectroscopy, and SEM.

From the mechanical properties [Fig.2] it was concluded that all of them are reduced significantly. Only with lower particle size (<200µm, after sieving) an increase of the mechanical properties was observed due to the etching caused by the acid pre-treatment (Figure 3). The effect on Young's modulus is clearly visible in [Fig.3]. The etching of the acid acts promoting mechanical adhesion, but also rigidizes the rubber by extracting the substances that may act as a plasticizer. The acid treated GTR particles have a rigid nature as it has been also observed in the studies by other authors [Cepeda 2000a] [Cepeda 2000b]. Then, GTR obtained with previous acid etching are usually stiffer than not treated ones. The sulpho-nitric mixture seems to provide the best results, but in general all acids have an improving effect. On the other hand, acidic pre-treatments were found to increase the tensile strength too. The effect of the acidic pre-treatment is related to the etching of the GTR surface, the elimination of moieties and additives and the achievement of a microporous surface more suitable for mechanical adhesion. The acid pre-treated samples showed similar behaviour, obtaining for the 50% sulphuric-nitric solution better results than the nitric or sulphuric acid pre-treatment, for the lowest particle size and highest GTR content. Low values for elongation at break and toughness were found in this case. The decrease of elongation at break is related to the imperfect interfacial adhesion between components. The

incidence of the poor adhesion between phases on this property is especially important. On the other hand, the compatibilizing effect achieved by the acid pre-treatments is counteracted by the increase of the stiffness of the rubber. The extraction of additives, oligomers or plasticizers of the GTR particles by the acid produces a rigid material. The reduction of the ability of deformation of the rubber influences the decrease of elongation and subsequently the decrement of the toughness.

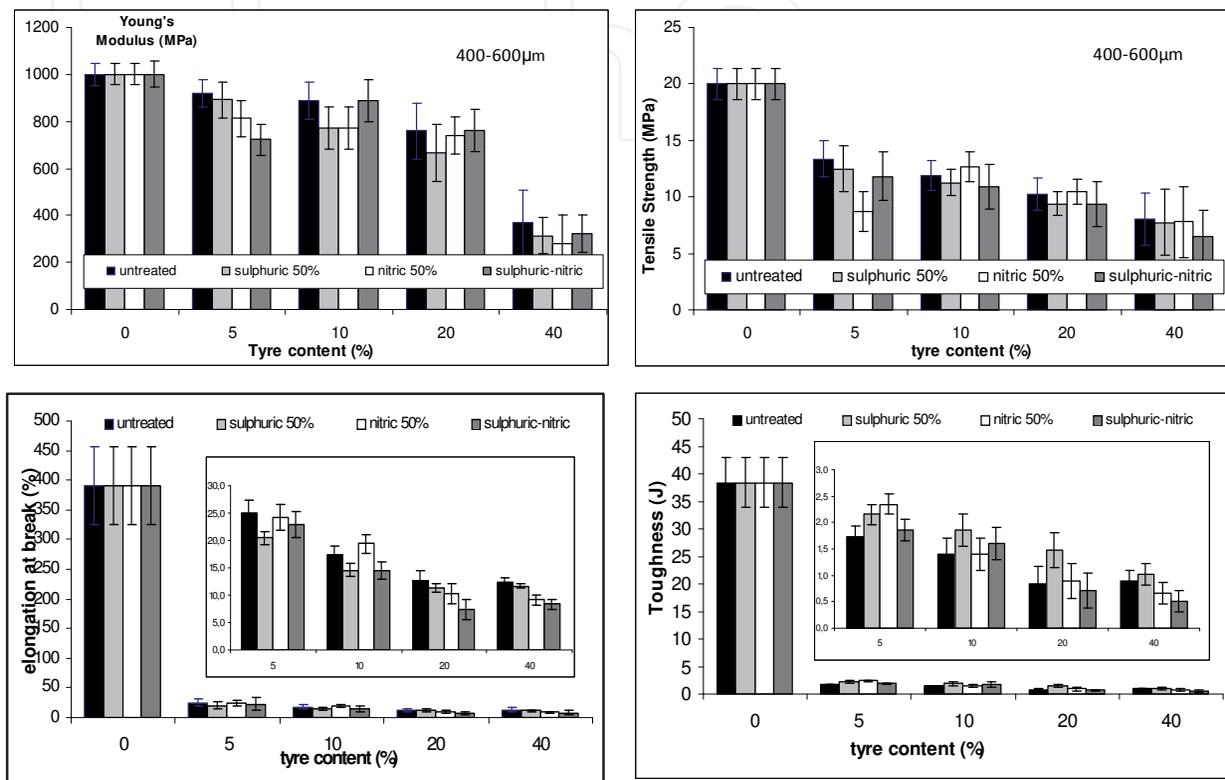


Fig. 2. Young's Modulus, tensile strength, elongation at break and toughness of composites based on treated GTR with particle size between 400-600µm and HDPE.

Chemical changes produced by acid treatments on GTR particles were studied by means of FTIR-ATR spectroscopy. Figure 4 shows a FTIR-ATR spectral area of 400-1800 cm^{-1} for the samples treated with H_2SO_4 and HNO_3 and compares these values to those for untreated GTR particles. To obtain this spectrum, it was chosen the band at 1026 cm^{-1} assigned to carbon black [Delor 1998] [Cañavate 2000] as a reference. The spectral analysis of untreated GTR shows a weak band at 1739 cm^{-1} that is associated to the thermal oxidation that occurs as a result of the exposure of the surface to oxygen (specially during the grinding handling), and which induces the formation of an oxidation skin that includes carbonyl groups. The strong band at 1640 cm^{-1} is associated to the C=C of polyisoprene, the weak band at 1540 cm^{-1} to zinc stearate (an anti-adherent compound), bands at 1430 cm^{-1} with the scissoring vibrations of =CH₂ (on butadiene), the band at 875 cm^{-1} with the trans isopropenyl unit (-C(CH₃)=CH-) and the band at 470 cm^{-1} with S-S.

The study shows that treating GTR particles with H_2SO_4 acid produces several chemical and degradative modifications on the tyre surface, mainly the formation of sulphonic acid, a decrease in double bonds (1640 cm^{-1}) due to the degradation process of polybutadiene and other unsaturated components of the tyre, and a decrease in content in minor components.

This phenomena may be related to the disappearance of the weak bands at 1739 and 1540cm^{-1} , the decreasing of bands at 1430 and 875cm^{-1} and the appearance of new bands at 1402 , 1121 and 618cm^{-1} , which is indicative of the $\text{O}=\text{S}=\text{O}$ stretching of the absorptions of sulphonic acid. These results are in agreement with previous studies [Cepeda 2000a] [Cepeda 2000b].

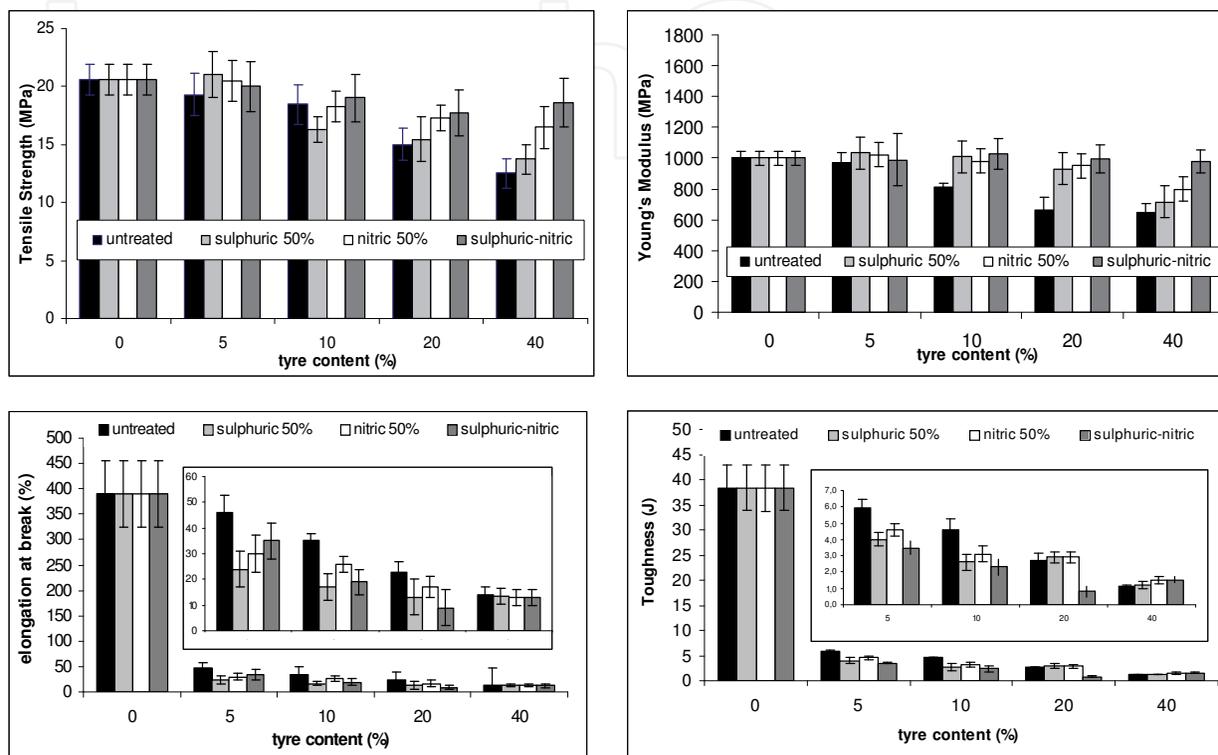


Fig. 3. Young's Modulus, tensile strenght, elongation at break and toughness of composites based on treated GTR with particle lower than $200\mu\text{m}$ and HDPE.

The treatment of GTR particles with nitric acid shows similar results to the sulphuric acid treatment except for the sulphur-oxygen derivatives. As shown in Figure 4, spectra of samples exposed to nitric acid show a decrease of the same bands as those exposed to sulphuric acid (1739 , 1640 , 1540 , 1430 and 875cm^{-1}), plus an increase of the band at 1382cm^{-1} assigned to $\text{N}-\text{N}=\text{O}$. The bands assigned to $\text{O}=\text{S}=\text{O}$ do not appear in this case. The observed chemical modifications agree with those presented in precius studies [Figovslq 1996] [Dierkes 2003]. Sulphuric acid acts as a strong dehydrating substance that can take up hydrogen and oxygen from organic matter and cause carbonisation. HNO_3 is also a powerful oxidizing agent when used in concentrated solutions. They modify the surface of the material introducing sulphur and nitrogen surface groups as $-\text{SO}_3$ and $-\text{NO}_2$. There is also an increase of groups as $\text{O}=\text{S}=\text{O}$ and $\text{C}-\text{SO}_2-\text{OR}$, a decrease of $\text{C}-\text{H}$ and an increase of $\text{C}=\text{C}$.

By the study of the spectrophotometry FTIR-ATR spectral bands, the main results obtained were following: i) every treatment studied produces a specific chemical modification on the ground tyre rubber particles, thus inducing the formation of specific groups; ii) several degradative effects appear in a similar way and do not depend on the acid used in the treatment (mainly the decrease in double bounds and the elimination of minor components and moieties).

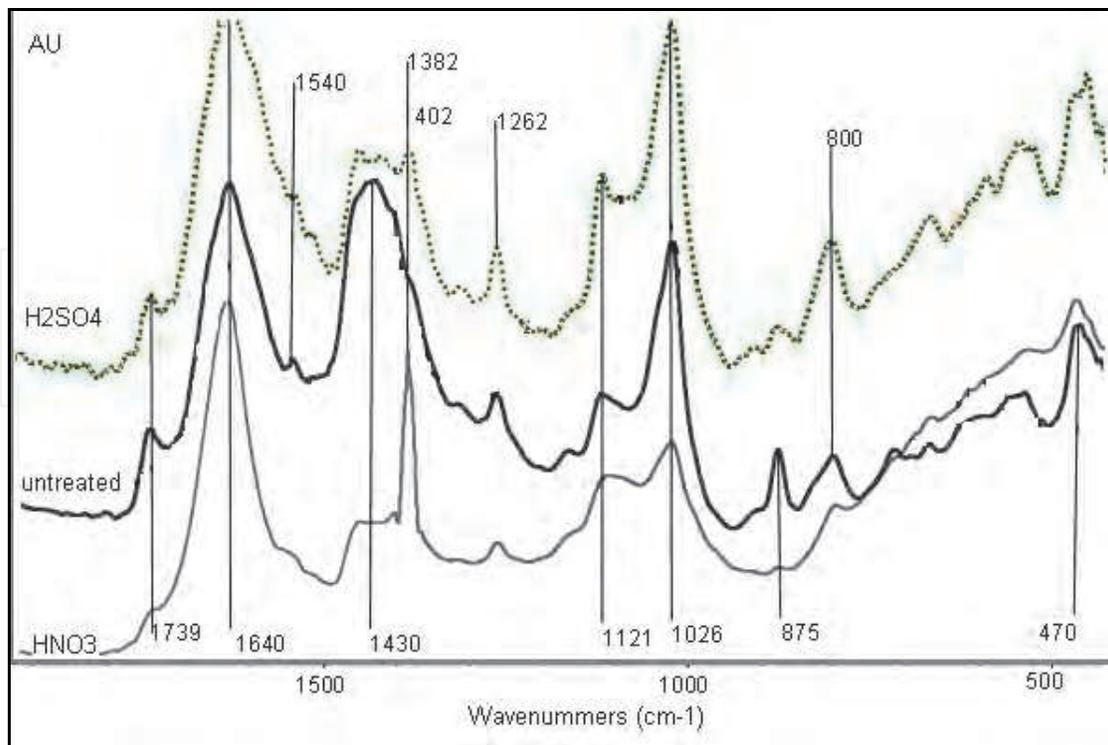


Fig. 4. Spectra of GTR particles: 1) treated with HNO_3 , 2) untreated and 3) treated with H_2SO_4 .

Some SEM microphotography pictures depicting the fracture surface of the GTR particles composites are shown in Figure 5. The images show different levels of magnification, which allows the comparison of the different particle sizes. The picture "a" shows a blend sample containing sulphuric treated GTR particles sizes between $400\text{-}600\mu\text{m}$. In the centre appears a big particle [see arrow 1], showing some cracks and pores big enough to be observed at this level of magnification. The particle is unlinked to the matrix, as it can be observed by the deep voids around its contour [see arrow 2]. The GTR seems to be resting on the HDPE, without being properly attached to it. On the other hand, the matrix has been strained and deformed plastically [see arrow 3]. Microphotography "b" from a sample including particles with sizes between $200\text{-}400\mu\text{m}$ pre-treated with HNO_3 shows similar features. The interaction between both components of the blends is not good and there are many cavities [see arrow 4] around the ground tyre rubber particle. Image "c" shows a different situation, since magnification is 10 times higher, particle is much smaller. The particle seems much more integrated in the matrix, and there is an area on the right with a clean cut that indicates that the particle itself has been broken instead of detached [see arrow 5], which proves the good performance of the interfacial contact, when the particles has been treated with H_2SO_4 . The contour of the particle does not show voids around, instead some fragments of HDPE sprout from the ground tyre rubber showing points of good attachment between both components [see arrow 6]. The high magnification allows the appreciation of the roughness achieved by the pre-treatment. Picture "d" shows particles (size between 200 and $400\mu\text{m}$) treated with $\text{H}_2\text{SO}_4\text{-HNO}_3$ (50%). Several medium size particles appear showing different levels of attachment.

The results of SEM and FTIR-ATR which are summarized above suggest that the surface modification of GTR particles influences their mechanical properties, and in some cases may also improve the interaction and compatibility between the HDPE matrix and the GTR.

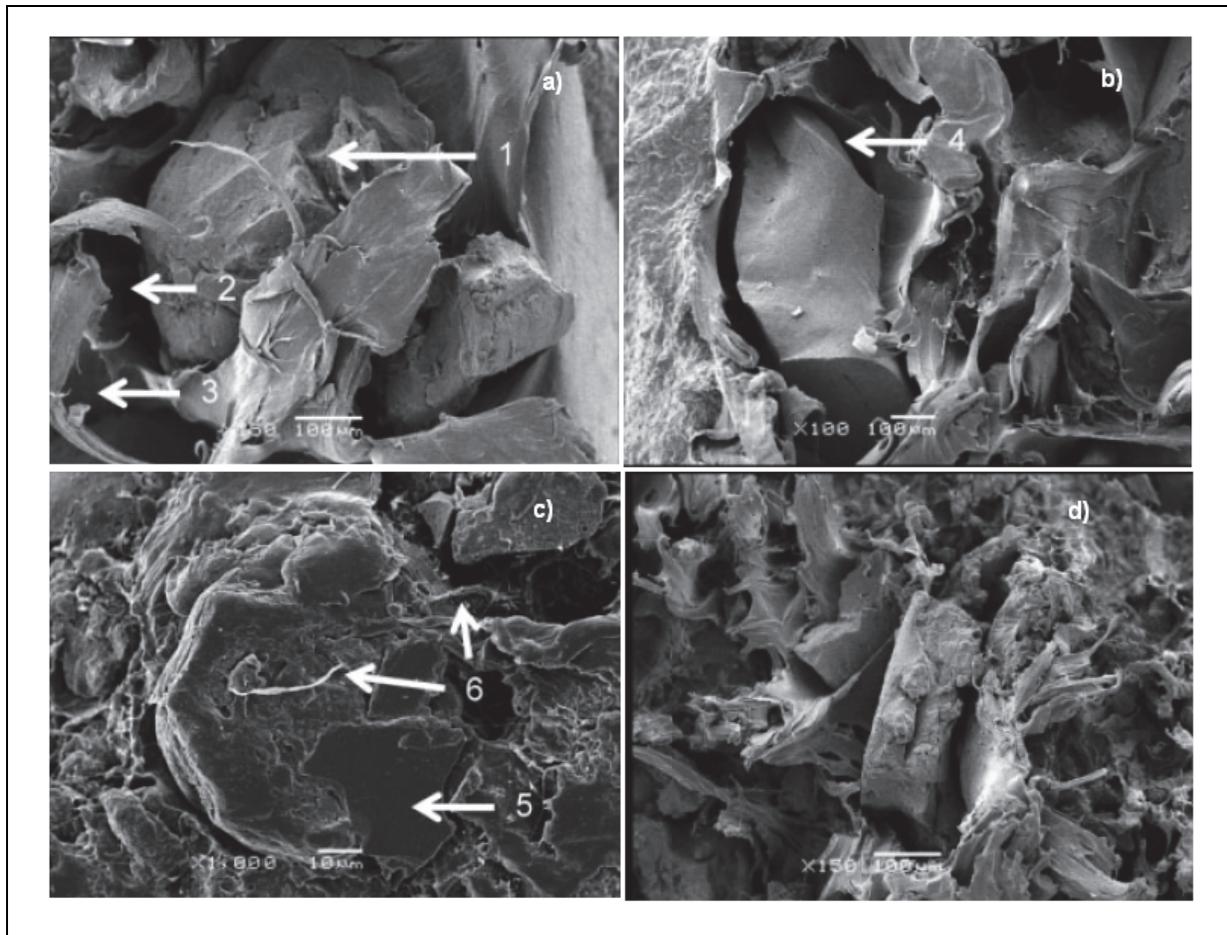


Fig. 5. SEM microphotographies of different fracture surfaces of GTR/HDPE components. a) particle size between 400-600 μm treated with H_2SO_4 , b) particle size between 200-400 μm treated with HNO_3 , c) particle size lower than 200 μm treated with H_2SO_4 , d) particle size between 200 and 400 μm treated with H_2SO_4 - HNO_3 (50%).

2.4 Use of waxes and wetting agents

K. Oliphant and W. E. Baker [Oliphant 1993] studied the influence of a coating layer process upon cryogenically GTR particles (CGTR). As a coating, they used Dow Primacor 3460, an ethylene acrylic acid (EAA) copolymer. They pre-treated the CGTR particles with the EAA copolymer. Afterwards the “coated” particles were added onto the melt LLDPE and HDPE matrixes. They observed that the deleterious effects of the CGTR particles is more pronounced in composites with HDPE than LLDPE. For example, the impact failure for pure LLDPE was seen to be a ductile yielding process in which the dart drawn the material out as it passes through. In contrast, the failure of the pure HDPE, although it involves some plastic deformation, is observed to occur through catastrophic propagation of a crack through the impact zone. This difference in impact failure was believed to be responsible for the poorer properties of the CGTR/HDPE composites. For LLDPE, where failure is ductile, large particles with moderate adhesion were easily tolerated but in CGTR/HDPE composites, the failure remained semi-brittle because particles were too large to induce brittle-to-ductile transition. Failure then occurs largely through crack propagation, and the large particles, even with moderate adhesion, act as serious flaws providing an easy path for

the crack to follow. They concluded that the addition of CGTR to a semi-brittle matrix requires much higher level of adhesion to retard crack growth at the particle/matrix interface, or much lower particle sizes to lower the brittle-ductile transition temperature. In their study they concluded that composites of 40 to 50% of precoated CGTR with LLDPE have impact properties approaching those of the pure LLDPE and retain adequate processability. This property improvement was believed to be due to an interaction between the carboxylic acid groups on the EAA copolymer with functional groups on the CGTR particles surface, which result in an increase on adhesion and greater ductibility. However, poor mechanical properties were obtained with CGTR/HDPE composites due to the semi-brittle nature of HDPE.

The mechanical properties of different composites of untreated GTR/HDPE are shown in Table 1. The increase of the GTR amount produces a decrease of the mechanical properties of the final composite. As commented before, this is due to a very weak adhesion between the two phases. The big particle size of the GTR and its crosslinked structure, which avoid any compatibility with the thermoplastic matrix, are the main reasons of this behaviour. The brittle response of the material is related to poorly adhering large particles present in the matrix [Bartczak 1999]. According to previous studies [Colom 2006], the composite with 20% of untreated GTR is a good compromise between mechanical properties and GTR content. Samples with higher percent of GTR are more difficult to process and show an excessive decrease in Young's modulus and tensile strength. The composition with 20% of GTR was used to study the effect of additives.

% GTR	Young's modulus (MPa)	Std. Dev.	Tensile strength (MPa)	Std. Dev.	Elongation at break (%)	Std. Dev.	Toughness (J)	Std. Dev.
0	927,90	27,95	20,67	2,22	390,08	22,20	38,4	3,00
10	889,00	24,94	16,44	1,53	17,31	1,31	1,57	0,23
20	759,65	33,11	14,34	2,13	12,55	1,46	1,13	0,21
40	370,25	12,84	8,74	1,72	12,00	1,73	0,88	0,15

Table 1. Mechanical properties of untreated GTR/HDPE composites.

The HDPE/Additives blends were prepared in order to analyze the influence of the additives in the mechanical properties of the matrix. Additive dosages are the same as those used in the mixture of HDPE with GTR particles. Table 2 shows the mechanical properties of HDPE with the different additives. In general, it is observed that additives decrease elongation at break and toughness but increase Young's modulus of HDPE. Tensile strength only increases with ester wax additive (Ceridust 5551) while it is lower with all the other additives. Hato and Luyt [Hato 2007] observed similar behaviour in terms of mechanical properties when they studied a blend of paraffin wax and HDPE. They explained the results in terms of morphology, suggesting a possible cocrystallization of the mixture HDPE/wax. According to their interpretation, wax chains are short enough (9nm compared to an approximate polyethylene lamellar thickness of 10nm) to be incorporated as straight chains into the HDPE lamellae. This incorporation occurs only at low dosages of wax. The cocrystallization would be responsible for the increase in Young's Modulus and the reduction in elongation at break. Blends of polyethylene (LDPE or LLDPE) with paraffin and oxidized paraffin waxes show similar properties [Krupa 2002].

% Aditive	Young's modulus (MPa)	Std. Dev.	Tensile strength (MPa)	Std. Dev.	Elongation at break (%)	Std. Dev.	Toughness* (J)	Std. Dev.
0	927,90	27,95	20,67	2,22	390,80	22,01	38,41	3,00
2.5% Dis-108	1.075,43	32,17	20,3	1,62	290,91	27,21	33,41	3,52
5% Byk-9077	1.087,04	24,13	19,53	2,61	317,42	36,01	32,62	4,44
2% Byk-Syn 2100	1.111,27	33,85	17,48	1,82	342,21	25,22	35,61	3,12
3% Byk-P 105	1.049,24	15,25	16,46	2,37	357,32	25,01	35,51	2,71
5% LPE520	1.088,26	17,48	16,94	3,14	337,66	15,90	34,47	1,61
5% LCPP1502	1.051,86	20,78	16,55	4,14	362,01	30,90	36,11	5,12
2.5% Ceridust 5551	1.248,99	36,01	22,19	2,15	266,21	16,61	33,00	3,12

Table 2. Formulations showing the influence of the additives on the mechanical properties of the matrix.

Table 3 shows the mechanical properties of the HDPE/GTR composites with the different additives. Disperbyk-108 and Byk-9077 are both designed to interact with acid groups and, as can be seen, do not improve any of the properties of the blend. It could be assumed then that GTR particles have a basic or rather a non polar surface. In order to improve interaction between a non polar surface and basic additives (such as Disperbyk-108 or Byk-9077) a synergic additive with acids groups can be used. As mentioned in section 4.3 Byk-Synergist 2100 has acid groups able to interact with the basic additives and with the non polar surfaces of the GTR particles, acting as a kind of "bridge". It can be observed that this additive causes a significant increase in elongation at break (13.2%). Byk-P 105, designed to interact with basic groups, is the wetting additive that most improves the mechanical properties of the composite. This result is related to carbon black characteristics. Carbon black is present on tyre formulations in form of furnace black pigments in amounts between 20 to 40%. As a result of the manufacturing process, furnace black pigments always contain small amounts of basic surface oxides (pyrone-like structures) [Buxbaum 1993]. The presence of these basic groups on the GTR particles surface could provide interaction with Byk-P 105. The wetting additive is anchored onto the ground tyre rubber particles surface and its non polar part is extended in the HDPE matrix. This wetting effect decreases the interfacial energy between the two phases and leads to a better adhesion. These results, obtained with an acidic wetting additive (Byk-P 105) are in concordance with the improvement in compatibility achieved by the ethylene-acrylic acid (EAA) in GTR/LLDPE composites attributed to the interaction between the acid groups on the EAA copolymer and CGTR particles surface [Oliphant 1993].

Licowax PE520 and Licocene PP1502 waxes also offer good mechanical properties, whereas the ester wax Ceridust 5551 reduces elongation at break and toughness. As discussed previously, there is an increase of Young's modulus and tensile strength when the ester wax is mixed with the matrix (Table 3). When GTR particles are included in the composite (Table 4), the same effect can be noticed. Despite this improvement, elongation at break and toughness drastically decrease. Therefore, the effect of Ceridust 5551 seems mainly related to the matrix, being unable to create the thin coating onto the GTR particles to improve adhesion. The effect of Licowax PE520 and Licocene PP1502 is also related to the zinc derivatives present in tyre formulations. Pastor et al. [Pastor 1994], Romero et. al [Romero 2001]. Monteiro et al. [Monteiro 2002] and Colom et al. [Colom 2009] observed a diffusion and migration of different tyre additives, like zinc derivatives from the bulk of different rubbers and reused tyres to their

surfaces. These additives lead to a poor adhesion between the GTR particles and the HDPE matrix due to its low free energy (unpolar properties). As mentioned before, waxes cover the particles reducing slightly the viscosity in the layers adjacent to the matrix. During calendaring at 150-155°C, zinc derivatives can be solubilised into the matrix due to the lower viscosity obtained by the waxes. This effect achieves a “cleaner” GTR particles surface that is easier to wet.

%Additive	Young's modulus (MPa)	Std. Dev.	Tensile strength (MPa)	Std. Dev.	Elongation at break (%)	Std. Dev.	Toughness* (J)	Std. Dev.
0	759,65	33,11	14,34	2,13	12,55	1,46	1,13	0,21
2.5% Dis-108	760,49	16,44	13,97	4,38	12,71	1,27	1,02	0,13
2.5% Dis-108 + 2% Byk-Syn 2100	737,05	18,69	13,98	2,88	14,19	2,33	1,24	0,11
5% Byk-9077	724,03	21,06	12,89	4,20	11,81	3,24	0,89	0,25
5% Byk-9077 + 2% Byk-Syn 2100	712,05	21,02	13,22	2,52	14,20	1,96	1,12	0,29
3% Byk-P 105	796,47	26,22	15,08	3,48	13,19	2,01	1,25	0,26
5% LPE520	797,10	31,44	15,55	1,84	13,69	2,33	1,32	0,19
5% LCPP1502	753,07	29,44	14,59	4,27	13,51	1,72	1,24	0,19
2.5% Ceridust 5551	846,16	27,23	14,66	2,80	11,04	1,56	0,94	0,14

Table 3. Influence of the additives on the mechanical properties of composites of 20% of GTR and 80% of HDPE.

Different percentages of GTR particles were tested with the wetting additive and waxes that gave best results (Byk-P 105, Licowax PE520 and Licocene PP1502). Table 4 shows the mechanical properties of the different composites.

Fracture surfaces of the composites containing the additives (Byk-P 105, Licowax PE520 and Licocene PP1502) that gave better mechanical properties were examined by SEM. Figure 6 contains SEM images of the composite with 20% of GTR particles and selected additives. Figure (a) shows the composite with 20% of GTR particles and 80% of HDPE without any additives, where GTR particles do not display any signs of adhesion to HDPE. Figures (b), (c), and (f) corresponding to the additives combination of 2.5% Disperbyk-108 + 2% Byk-Synergist 2100, 5% Byk-9077 + 2% Byk-Synergist 2100 and 5% Licocene PP1502 respectively, show also poor interaction. Figure (d) corresponds to the composite including 3% of Byk-P 105: the particle is surrounded by the HDPE matrix but the picture does not show a perfect interaction. On the other hand, photograph (e) with 5% of Licowax PE520 shows good adhesion between the two phases. The existence of some filaments protruding from the GTR particles indicates a strong interaction.

Four samples of each specimen were examined under the microscope for dispersion quality study. The mechanical energy provided by the two roll mill during the milling stage breaks the GTR agglomerates and creates smaller particles with larger interfaces in contact with the thermoplastic matrix. Wetting additives and waxes improve dispersion stability of single GTR particles; consequently, better mechanical properties can be achieved.

% of GTR	% of additive	Young's modulus (MPa)	Std. Dev.	Tensile strength (MPa)	Std. Dev.	Elongation at break (%)	Std. Dev.	Toughness* (J)	Std. Dev.
10%	No additive	889,00	24,94	16,44	1,53	17,31	1,31	1,57	0,23
10%	3% Byk-P 105	914,94	36,54	16,86	2,58	17,61	2,71	1,65	0,26
10%	5% LPE520	933,27	17,48	16,91	2,80	14,86	2,59	1,59	0,16
10%	5% LCPP1502	906,25	30,78	16,44	3,91	17,62	3,41	1,60	0,32
20%	No additive	759,65	33,11	14,34	2,1	12,55	1,4	1,13	0,21
20%	3% Byk-P 105	796,47	26,22	15,08	3,48	13,19	2,01	1,25	0,26
20%	5% LPE520	797,10	31,44	15,55	1,84	13,69	2,33	1,32	0,19
20%	5% LCPP1502	753,07	29,44	14,59	4,27	13,51	1,72	1,24	0,19
40%	No additive	370,25	12,84	8,74	1,72	12,00	1,73	0,88	0,15
40%	3% Byk-P 105	427,10	15,92	8,46	2,70	13,92	1,25	0,90	0,05
40%	5% LPE520	421,39	22,41	9,3	1,82	14,97	2,04	0,92	0,14
40%	5% LCPP1502	405,25	17,64	8,29	2,95	11,81	1,61	0,54	0,16

Table 4. Influence of the additives on the mechanical properties of composites of 20% of GTR and 80% of HDPE.

Figure 7 shows four pictures. (a) and (b) correspond to the composites without additives and with 2.5% Disperbyk-108 + 2% Byk-Synergist 2100 respectively. Both pictures show the existence of agglomerates, which can be seen as GTR particles in contact along their edges with its interstitial spaces filled with the HDPE matrix. On the other hand, pictures (c) and (d) correspond to 3% of Byk-P 105 and 5% of Licocene PE520 respectively; both show single GTR particles surrounded by the HDPE matrix. This lack of agglomerates means a better dispersion and stabilization of the particles, and consequently an improvement on the mechanical properties of the final blend.

From the study of the mechanical properties, the following conclusions can be drawn:

- i. the increase of the GTR particles amount in neat composites produces a decrease of the mechanical properties in the final composite, especially in elongation at break and toughness. The mixture with 20% of GTR particles gives a balanced compromise between the amount of GTR particles and good mechanical properties;
- ii. the wetting additive Byk-P 105 and the wax Licowax PE520 give the best performance in the blends with 10, 20 and 40% of ground tyre rubber particles;
- iii. all additives produce an increase in the Young's modulus and tensile strength of the HDPE matrix. This increase is attributed to cocrystallization of the waxes with HDPE.

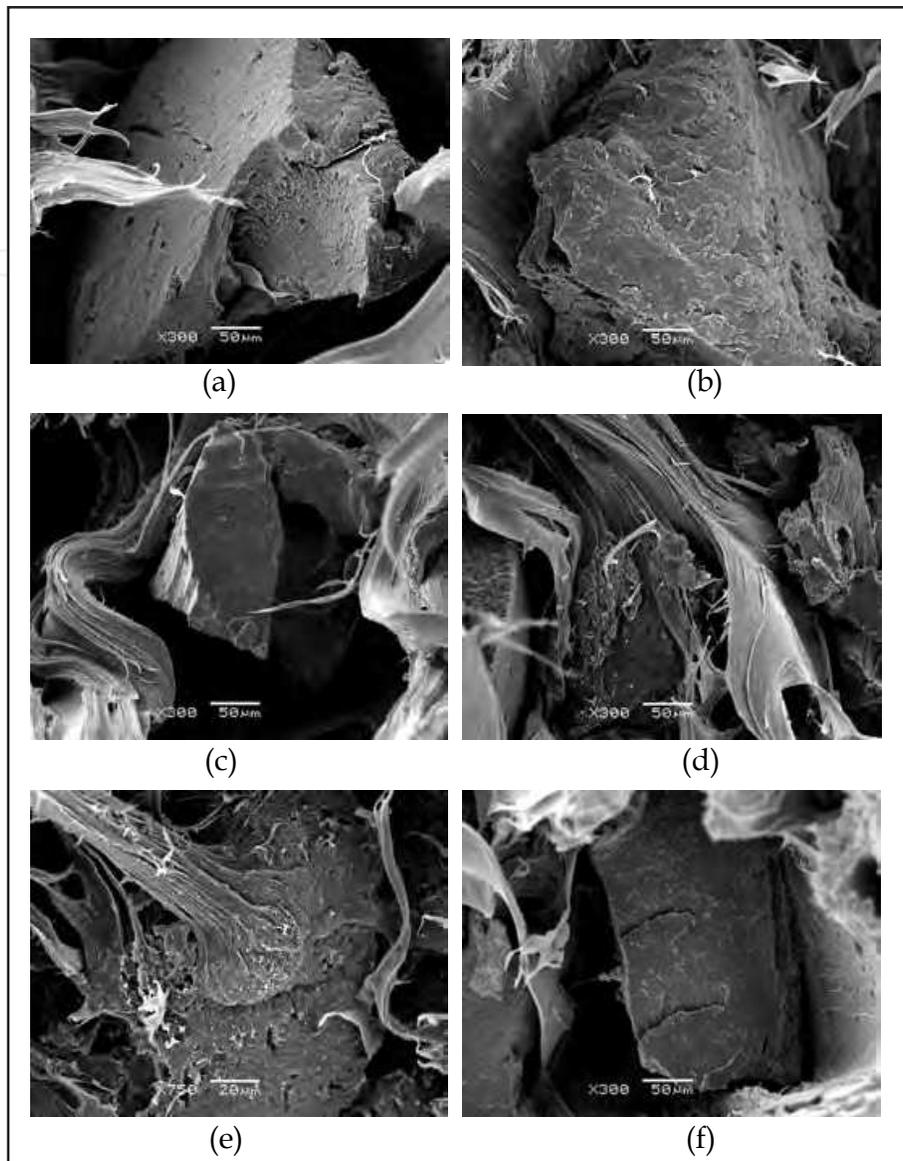


Fig. 6. SEM microphotographs of the composites 20% of GTR and 80% of HDPE with different additives. a) neat composite, b) 2.5% Dis-108 + 2% Byk-Syn 2100, c) 5% Byk-9077 + 2% Byk-Syn 2100, d) 3% Byk-P 105, e) 5% LPE520 and f) 5% LCPP1502.

Licowax PE520 acts adequately promoting adhesion. Fracture surface reveals fragments of HDPE attached to the particles. On the other hand the Byk-P 105 image shows particles better wrapped in thermoplastic than with any other wetting additive. Optical microscope's photographs show that samples including Byk-P 105 and Licowax PE520 contain fewer agglomerates. The homogeneous dispersion of the GTR particles in the matrix produces

2.5 Formulations of thermoplastics vulcanizates

TPVs based on EPDM and PP or HDPE are the most representative example of this kind of materials. They are used for automotive applications, like bumpers or hoses, and in other uses such as covering wires, pipes, boots, handle tools, etc. [Van Duin 2006].

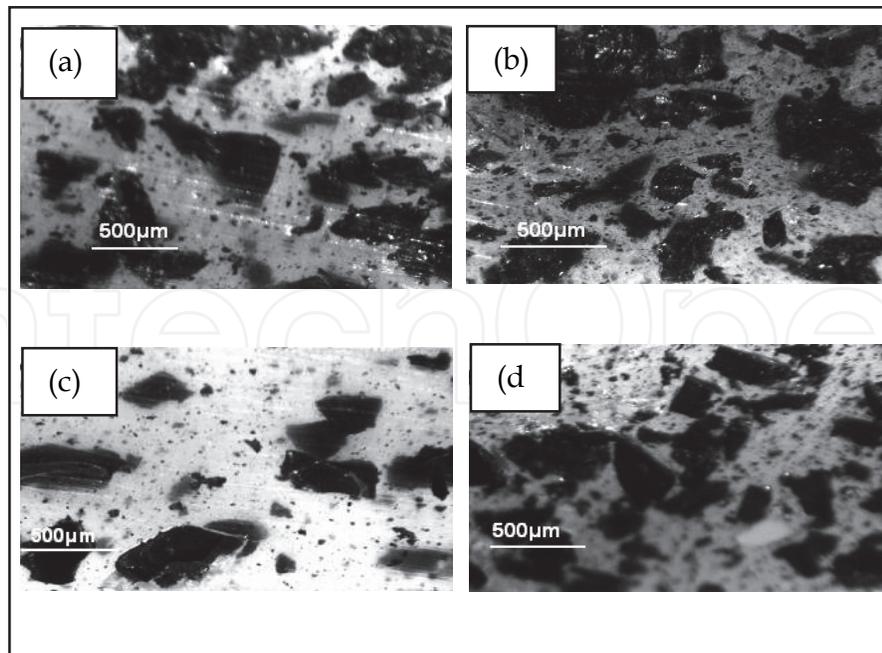


Fig. 7. Microscope pictures of the composites with 20% of GTR and the following additives: a) neat mixture, b) 2.5% Dis-108 + 2% Byk-Syn 2100, c) 3% Byk-P 105 and d) 5% LPE520.

Their thermoplastic nature allows them to be reprocessed. On the contrary, rubber articles, like tyres, are not recyclable or re-processible due to their vulcanized structure. However, the increasing price of EPDM over the last decade has led to its substitution by metallocene-based ethylene-octene and ethylene-butene elastomers [Sherman 2008]. Therefore, the attempt to substitute as much EPDM as possible by GTR in a TPV formulation could be considered a good option for cost reduction of the final formula and as an upcycling application for GTR.

Over recent years, some attempts to use GTR in TPV's formulations have been made. [Kumar 2002] studied the feasibility of producing TPE with Low Density Polyethylene (LDPE), fresh rubber (SBR, NR or EPDM) and mechanical degraded GTR (with and without processing oil). [Punnarak 2006] reported the study of composites based on reclaimed tyre rubber (RTR) and HDPE, dynamically vulcanized with sulphur, maleic anhydride (MA) and dicumyl peroxide (DCP), [Naskar 2001] presented a TPE made of cryogenic GTR, EPDM and ethylene-co-acrylic acid, vulcanized with DCP. Other studies have been published with GTR pre-treated with bitumen, which according to the authors, contributes to the GTR devulcanization, also acting as a plasticizer and compatibiliser in the composites. From these published works, it can be concluded that the addition of fresh EPDM with good matrix compatibility (similar surface energies) produces an effect of encapsulation of the GTR particles, creating a co-continuous phase and improving the adhesion between phases. There are several factors that influence the final properties, like plastic/rubber composition, mixing conditions, and type of curing agent used to crosslink the elastomeric phase. This section reports the study of a TPV based on EPDM, standard injection HDPE and GTR, dynamically crosslinked with peroxides. Peroxides are fundamental in the final TPV properties. A new peroxide, 3,3,5,7,7-pentamethyl-1,2,4-trioxepane, developed by Akzo Nobel Polymer Chemicals (Trigonox 311) was used in the present study. Unique about Trigonox 311 is its decomposition temperature, which is significantly higher compared to

any other commercially available crosslinking peroxides, allowing processing temperatures of 180-190°C with no scorch problems.

The most important factors that affect thermoplastic vulcanizates morphology and mechanical properties are: a) type of curing agents used to crosslink the elastomeric phase, b) plastic/rubber composition (including EPDM/GTR proportion on the rubber) and c) degree of crosslinking. Four different experimental sets were designed in order to perform an accurate study of the thermoplastic vulcanizates mechanical properties. The first set was carried out on composites 40/30/30 (HDPE/EPDM/GTR) with peroxide contents from 0.1 to 3% using Trigonox 311 (Table 6). The influence of the Trigonox 311 content on thermoplastic vulcanizates mechanical properties was studied. In order to assess the previous results, a second set of samples containing only DCP was tested. Different temperatures of curing, related to peroxides activity, were examined too (Table 7). Moreover, the influence of the plastic/rubber composition of the composites was tested at constant EPDM/GTR ratio and peroxide content (Table 7). Finally, GTR was substituted at different concentrations by EPDM in a fixed plastic/rubber and peroxide content composition (Table 8). These last sets of samples were tested in order to determine the amount of EPDM that can be replaced by GTR particles maintaining a good balance of mechanical properties of the thermoplastic vulcanizates.

Table 5 shows the influence of the peroxide content on the mechanical properties of composites where the plastic/rubber and EPDM/GTR ratios were kept constant at 40/60 and 50/50 respectively. A reference sample without EPDM and without peroxide (only HDPE/GTR) is also included showing a brittle performance (composite n°1, Table 5). When EPDM is incorporated to the composite, elongation at break and toughness increase immediately, however, Young's modulus and tensile strength decrease due to the incorporation of a rubber-like phase. As peroxide content increases, all properties show higher values due to crosslinking, but at higher contents of Trigonox 311 (2 and 3%) elongation at break start decreasing. This could be related to the reaction of the peroxides with the thermoplastic matrix, because they are not selective for unsaturated elastomers. Similar results were reported in previous studies [Kumar 2002]. In polymer composites, an increase in elongation at break is directly related to a better compatibility between phases. Therefore it can be concluded that composite 6, containing 1% of Trigonox 311, shows maximum elastomeric thermoplastic properties. In other words, from this experiment, 1% of Trigonox produces the best results to crosslink EPDM and seems to be effective creating a network to encapsulate ground tyre rubber particles.

Processing conditions are important issues regarding final properties of the cured composite. DCP, as standard peroxide for TPV's studies, was also tested in combination with Trigonox 311, in order to study synergetic effects and compare processing and physical properties of the composites. Although 1% of Trigonox showed maximum performance in the first study, the content was reduced to 0.5% when adding DCP as additional peroxide, in order to avoid excess of peroxide. That would be also beneficial for cost savings. Table 6 shows the mechanical properties of the DCP alone and in combination with Trigonox 311, at different processing temperatures. Composite 9, with 0.1% of DCP, was consolidated at 170°C and did not show difficulties in handling. However, its properties were not as good as those of composite 6. Composites with higher DCP contents lead to premature crosslink in the two roll mixer (working temperature 150-155°C) and those pressed at higher temperatures became very sticky and difficult to remove from the press being impossible to

measure. The synergy effect of both peroxides at 210, 190 and 180°C was studied in composites 10, 11 and 12. Consolidation temperature seems to have an important role in the final properties. Different conditions for composites containing 0.5% of Trigonox and 0.1% of DCP were tested. Composite 10 was difficult to take off the press too but composites 11 and 12 showed no handling problems. Composite 11 shows better elongation at break and toughness than 6. Therefore a combination based on 0.5% of Trigonox and 0.1% of DCP respectively seems to give the maximum elastomeric thermoplastic properties. Nicolini et al. [Nicolini 2006] also found that the mixture of two curing agents, DCP/bismaleimide, in TPVs based on PP/EPDM 35/65 w/w gave the best mechanical properties and much better ones than DCP alone.

The plastic/rubber composition has also an important influence in the final material properties. Table 7 shows the mechanical properties of composites where EPDM/GTR ratio was kept constant at 1:1, and peroxide combination of 0.5% Trigonox 311 and 0.1% DCP. As HDPE content increases from 10 to 40%, Young's modulus, tensile strength and toughness gradually increase too. Elongation at break decreases due to the incorporation of a plastic phase. With even higher contents of HDPE (more than 50%), Young's modulus and tensile strength increase while elongation at break and toughness decrease. The higher the HDPE content the less toughening effect of the elastomeric phase. Therefore the mixture with 40% of HDPE and 60% of rubber phase shows the highest desired properties. Similar results were found by A. K. Naskar et al. [Naskar 2001]. The last set of samples study mechanical properties when fresh rubber is replaced by GTR particles. Up to this point, the best properties have been obtained with the 40/60 composition of plastic/rubber phase. Therefore, the HDPE phase and peroxide content are maintained while EPDM content is varied from 60% to 0%. Table 8. shows the results. When GTR particles content increased the loss in mechanical properties due to the incompatibility between GTR particles and HDPE is clear. From 60% to 30% of EPDM, the composite becomes gradually less toughened but when 40% of GTR particles is included, EPDM seems to lose its encapsulating and compatible effect leading to an important decrease of elongation at break and toughness. It's interesting to notice that the composite with 60% of GTR particles is even more brittle than the one containing 10% of EPDM. It seems that peroxides only vulcanizes EPDM and do not react with the possible existing active sites of GTR.

After this study an overall vision of composites behaviour is acquired. In order to assess the substitution of EPDM for GTR, two composites are selected for comparison. Composite 23 does not contain GTR (40%HDPE + 60%EPDM + 0.5%Trig + 0.1%DCP) and composite 26 has 30% of EPDM substituted by GTR (40%HDPE + 30%EPDM + 30%GTR + 0.5%Trig + 0.1%DCP). Results show (Table 8.) that even with the considerable amount of 30% in GTR particles, the 297% value in elongation at break fulfils the major criteria for a thermoplastic elastomer: which this value must be higher than 100%. However, if the GTR particles amount is increased to 40% the elongation at break drastically drops down to 121% which is almost in the limit. Therefore, 30% of GTR in the composite is the optimum amount for the desired balance: maximum GTR particles quantity with acceptable mechanical properties.

Figure 8 shows an increasing hardness tendency when peroxide dosage (Trigonox) is increased in the blends where the plastic/rubber and EPDM/GTR ratios were kept constant at 40/60 and 50/50 respectively. Figure 9 shows the effect on hardness, when EPDM is substituted by GTR (Table 8). At high GTR dosages, from 40 to 60%, the hardness value is maintained constant at values of 89-90, in those cases, EPDM (less than 20%) is not able to

form the co-continuous phase to encapsulate the dispersed GTR particles and give the rubber-like property on the final blend. This is in concordance with the results obtained in the mechanical properties, where composites with less than 30% of EPDM suffer an important decrease in elongation at break and toughness.

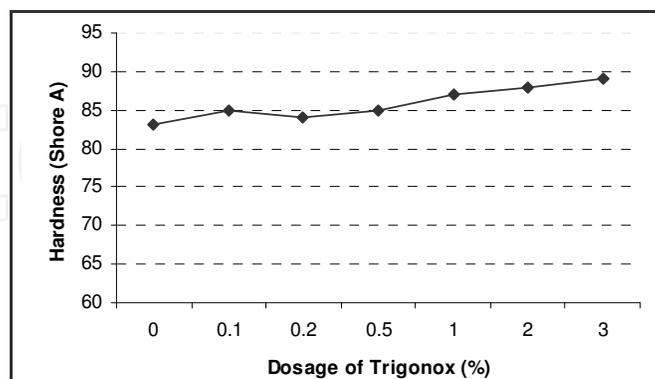


Fig. 8. Hardness as function of Trigonox dosage

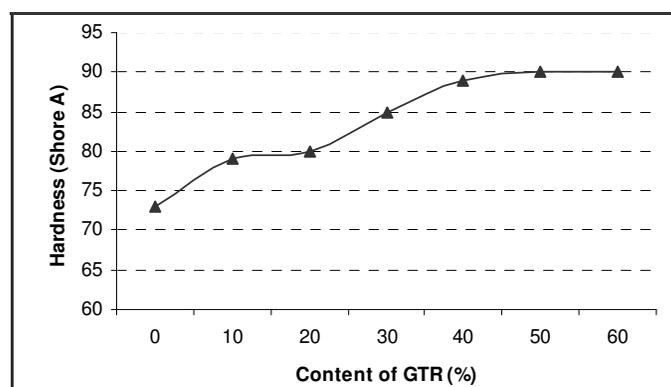


Fig. 9. Hardness as function of GTR dosage.

ATR-FTIR spectroscopy was used to study the chemical changes involved after dynamic vulcanization. The main peroxides reaction consists on the hydrogen atoms abstraction from the polymer chain and formation of the corresponding macroradicals. The reactivity of the generated free radicals depends on the hydrogen bond dissociation energy [Naskar 2004]. Trigonox 311 major decomposition products are methane, acetone, isopropyl acetate, 3-hydroxy-1,3-dimethylbutyl acetate and 3-oxy-1-methylbutyl acetate, while, major DCP decomposition products are methane, acetophenone, 2-phenylpropanol-2, α -methylstyrene and water. Peroxide cross-linking of unsaturated rubbers and polymers is achieved via free-radical mechanism that involves three steps: the first is the generation of radicals by thermal decomposition of the peroxide, on second place the radical attack on the polymer chain via hydrogen abstraction to generate polymer radicals, and third and last, the combination of two polymer radicals to form carbon-carbon crosslinks. In order to investigate the chemical changes on composites with Trigonox 311, the sample's spectra with constant 40/30/30 ratio of HDPE/EPDM/GTR and an increasing peroxide dose from 0 to 3% were examined.

Composite	% of HDPE	% of EPDM	% of GTR	% of Trigonox 311	Young's Modulus (MPa)	Std. dev %	Tensile Strength (MPa)	Std. dev %	Elongation* at break (%)	Std. dev %	Toughness* (J)	Std. dev %
1	40	0	60	0	440.45	14.80	9.56	0.23	12.88	1.92	1.03	0.12
2	40	30	30	0	98.99	6.00	5.12	0.25	153.03	21.63	8.93	2.13
3	40	30	30	0.1	116.91	10.80	5.1	0.23	145.98	34.81	8.69	2.84
4	40	30	30	0.2	126.71	9.70	5.32	0.42	170.14	40.03	8.90	2.01
5	40	30	30	0.5	120.99	4.60	5.6	0.22	190.19	32.72	9.35	2.32
6	40	30	30	1	126.71	4.45	5.85	0.12	268.36	29.15	11.34	1.31
7	40	30	30	2	128.26	7.61	6.22	0.15	260.93	29.21	11.08	1.33
8	40	30	30	3	130.83	6.43	6.55	0.95	228.53	48.43	10.73	5.32

Table 5. Mechanical properties of the composites containing HDPE/EPDM/GTR ratio of 40/30/30 and different contents of Trigonox 311. The table includes the composite of 40% HDPE with 60% GTR.

Composite	% of HDPE	% of EPDM	% of GTR	% of Trigonox 311	% of DCP	Temperature (°C)	Young's Modulus (MPa)	Std. dev %	Tensile Strength (MPa)	Std. dev %	Elongation* at break (%)	Std. dev %	Toughness* (J)	Std. dev %
9	40	30	30	0	0.1	170	116.26	6.12	6.98	0.23	221.94	21.52	13.91	1.22
10	40	30	30	0.5	0.1	210	94.98	10.01	4.99	0.81	156.24	24.74	7.03	3.93
11	40	30	30	0.5	0.1	190	97.51	5.32	7.06	0.67	297.33	30.62	17.17	3.52
12	40	30	30	0.5	0.1	180	90.34	8.49	6.74	0.42	281.41	28.91	15.86	4.01

Table 6. Mechanical properties of the composites containing HDPE/EPDM/GTR ratio of 40/30/30 with 0.1% of DCP and mixtures of 0.1% DCP + 0.5% Trigonox 311, at different temperatures.

Composite	% of HDPE	% of EPDM	% of GTR	% of Trigonox 311	% of DCP	Young's Modulus (MPa)	Std. dev %	Tensile Strength (MPa)	Std. dev %	Elongation at break (%)	Std. dev %	Toughness* (J)	Std. dev %
13	10	45	45	0.75	0.15	9.78	0.21	2.45	0.21	360.00	35.02	8.33	1.9
14	20	40	40	0.67	0.13	23.75	1.43	4.00	0.42	337.00	44.81	12.72	2.1
15	30	35	35	0.58	0.11	55.49	4.52	6.04	0.51	293.42	48.23	15.31	2.3
16	40	30	30	0.5	0.1	97.51	5.32	7.06	0.67	297.33	30.62	17.17	2.5
17	50	25	25	0.42	0.08	209.00	12.23	7.10	0.31	135.00	12.31	9.04	0.7
18	60	20	20	0.33	0.07	263.15	18.81	8.25	0.22	107.70	24.21	7.91	4.9
19	70	15	15	0.25	0.05	385.52	16.62	10.44	0.41	154.63	45.01	5.68	4.9
20	80	10	10	0.17	0.03	637.47	14.61	14.59	0.51	42.26	10.83	3.51	1.3
21	90	5	5	0.08	0.01	783.07	60.61	16.70	0.44	30.80	7.82	2.70	1.4
22	100	0	0	0	0	927.90	27.91	17.17	0.52	390.80	22.01	38.41	3.0

Table 7. Mechanical properties of formulations showing variation of the rubber/plastic composites at fixed peroxide dose and constant EPDM/GTR ratio of 1:1.

Composite	% of HDPE	% of EPDM	% of GTR	% of Trigonox 311	% of DCP	Young's Modulus (MPa)	Std. dev %	Tensile Strength (MPa)	Std. dev %	Elongation at break (%)	Std. dev %	Toughness* (J)	Std. dev %
23	40	60	0	0.5	0.1	41	2.32	14.22	0.53	751.21	18.84	54.61	3.46
24	40	50	10	0.5	0.1	65.59	6.95	10.92	0.53	592.65	19.14	39.42	2.36
25	40	40	20	0.5	0.1	89.19	11.84	7.26	1.14	417.68	32.68	22.89	3.98
26	40	30	30	0.5	0.1	97.51	5.32	7.06	0.67	297.33	30.62	17.17	2.52
27	40	20	40	0.5	0.1	132.93	10.19	6.14	0.16	121.38	22.27	6.3	1.61
28	40	10	50	0.5	0.1	161.37	14.36	6.23	0.42	33.54	11.75	1.72	0.72
29	40	0	60	0.5	0.1	172.42	10.32	6.33	0.45	25.78	4.46	1.24	0.32

Table 8. Mechanical properties of the 40:60 plastic:rubber composites at different rubber (EPDM:GTR) ratios.

In Figure 10 can be seen, the presence of different C=O stretching bands (1744, 1592, 1586 cm^{-1}) associated to carbonylated products such as ketones, aldehydes or other products that can be generated by the Trigonox 311 decomposition. The C=O peak intensity is observed to be higher for the composites cured with higher peroxide amount, indicating an oxidative degradation of the matrix polymer due to the higher peroxide concentration.

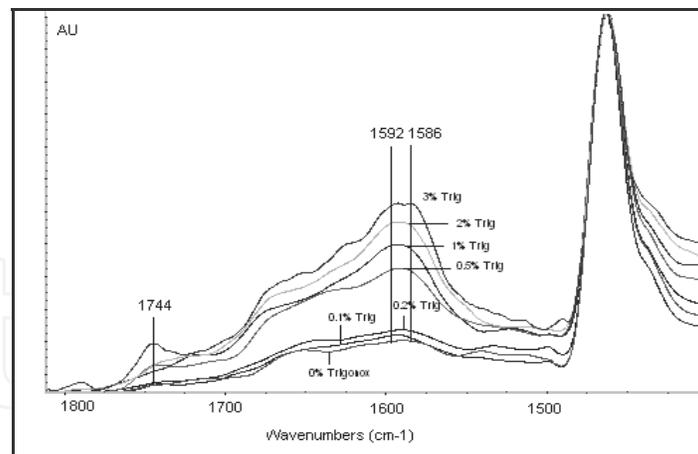


Fig. 10. ATR-FTIR spectres of samples with HDPE/EPDM/GTR ratio of 40/30/30 and an increasing peroxide dose (from 0 to 3%) for the area between 1800 and 1400 cm^{-1} .

Figure 11 shows the spectra between 1400 and 1000 cm^{-1} . Bands at 1374, 1258, 1090 and 1025 cm^{-1} are assigned to the asymmetric stretching vibrations of C-O-C bonds of esters and ethers linkages during the curing reaction between peroxide free radicals and the polymeric macroradicals. The C-O-C band absorbance increases up to 1% of Trigonox but it decreases at higher peroxide dose (2 and 3%) due to the preferred oxidative degradation reaction of the peroxide with the matrix. The results are in concordance with the mechanical properties, where the composite with 1% of Trigonox showed the more interesting mechanical behaviour.

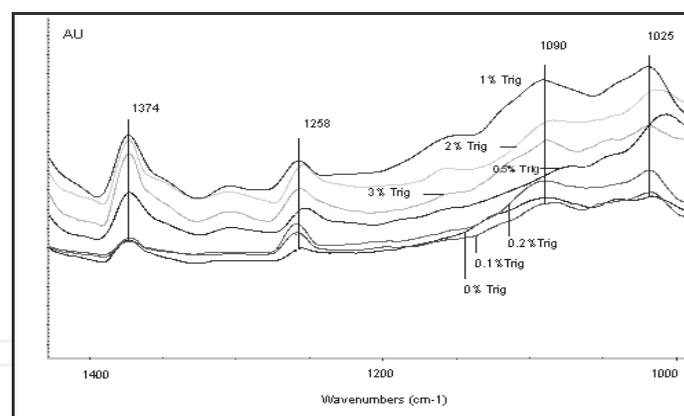


Fig. 11. ATR-FTIR spectres of samples with HDPE/EPDM/GTR ratio of 40/30/30 and an increasing peroxide dose (from 0 to 3%) for the area between 1400 and 1000 cm^{-1} .

Figure 12 shows SEM micrograph of fracture surface of the composite without EPDM and peroxides, only HDPE and GTR. These two materials are incompatible due to their different chemical composition as can be seen in picture 12.a where GTR particles appear almost isolated without being wet by the HDPE matrix. Without any kind of compatibility between the two materials, very little adhesion is possible, leading to very poor mechanical properties as already described.

The influence of EPDM addition into the HDPE-GTR composite is shown in picture 12.b. The addition of an elastomeric component which, at the same time contains high amount of

polyethylene should help to improve compatibility between HDPE and GTR particles. Particles are not as isolated as in the composite without EPDM. However, can be observed as some GTR particles parts are still not surrounded neither by HDPE nor EPDM. In other words, EPDM still is not able to encapsulate all GTR particles.

As expected, the encapsulation effect is seen in Figures 12c and 12d with peroxides addition. In both pictures can be observed how GTR particles are encapsulated by EPDM. In the case of Figure 12d corresponding to the composite with 0.5%Trigonox + 0.1%DCP, the encapsulating effect is much more visible. The fact that GTR particles are completely encapsulated means that EPDM has formed a three-dimensional network within them, and at the same time, EPDM creates a co-continuous phase with HDPE. This effect leads to a much better adhesion and better mechanical properties as already observed.

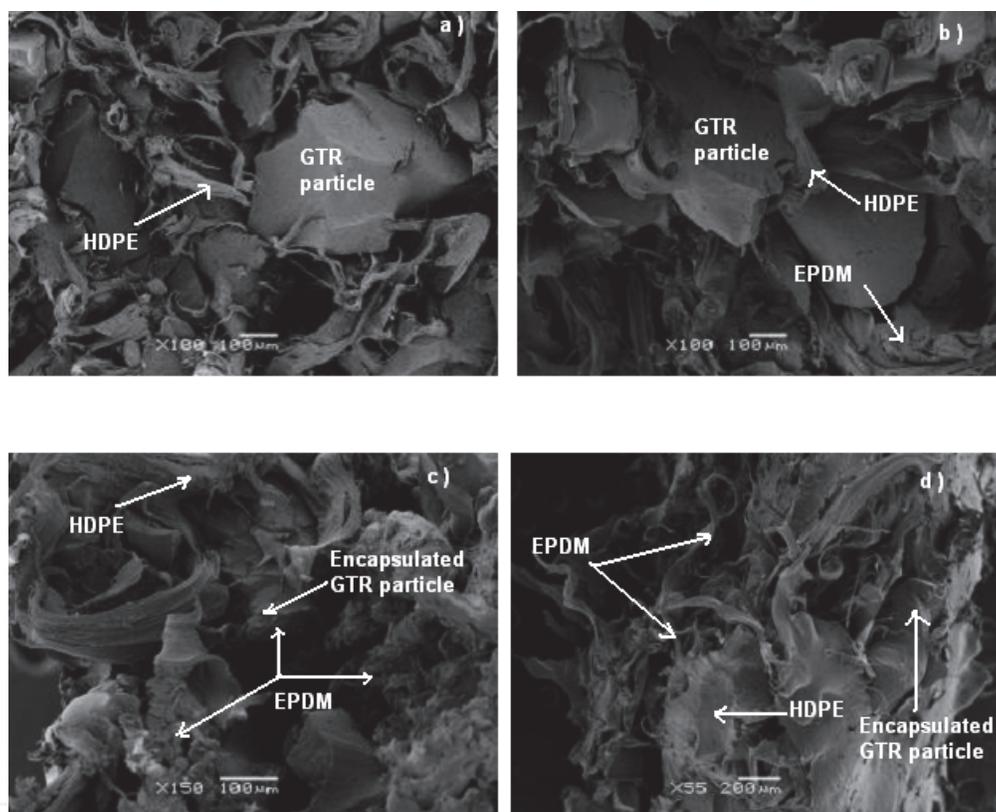


Fig. 12. Shows the SEM micrograph of the following composites: (a) 40%HDPE 60%GTR, (b) 40%HDPE 30%EPDM 30%GTR, (c) 40%HDPE 30%EPDM 30%GTR 3%Trigonox and (d) 40%HDPE 30%EPDM 30%GTR 0.5%Trig 0.1%DCP.

The following conclusions can be drawn from this section: i) The composition consisting on 40% HDPE 30% EPDM 30% GTR 0.5% Trigonox 311 and 0.1% DCP gives the best balance regarding GTR amount (30%) and mechanical properties. It is proved that process conditions, such as press temperature, have an important role in the final mechanical properties. The mixture of two different peroxides types give the best synergist effect. High peroxide amount has a negative impact on crosslinking due to a possible thermooxidative degradation of the thermoplastic matrix as observed by FTIR-ATR analysis. ii) The encapsulation phenomena of EPDM over GTR particles can be observed in SEM pictures. An optimization of composite components for maximum adhesion between GTR particles

and HDPE matrix is studied during the mechanical properties test. Good adhesion is only possible if GTR particles are encapsulated by fresh rubber, i.e. EPDM. Good adhesion between phases is directly translated as good mechanical properties in the final composite. GTR can be up-cycled if is used as a rubber component in TPV production. In the present study, 30% of fresh rubber can be substituted by this recycled material, still fulfilling the major criteria for this kind of materials.

3. Conclusion

After the complete study of the three compatibilization methods and the comparison of the mechanical properties, estimation costs, maximum amount of GTR particles and easiness of production of the final compound, the following final conclusions can be taken:

- A detailed study of the composites obtained by each compatibilization method was done. In the three methods there has been a mechanical properties study, a chemical and morphological study.
- The effectiveness of the compatibilization method can be check with mechanical properties of the blends. Mechanical properties are method dependant.
 - Acid treatment does not improve any of the properties with the chosen particle size. The acid causes etching on the surface of GTR particles improving, in this way, mechanical adhesion. A brittle performance of the compound can be observed at lower particle size ($< 200\mu\text{m}$).
 - Addition of waxes and wetting additives has a slightly improvement of all mechanical properties. The best results were obtained with the wetting additive Byk-P 105 and the wax Licowax PE 520. Byk-P 105 interacts with the basic groups present in the GTR particles surface. Licowax PE 520 acts covering the GTR particles and reducing slightly the viscosity in the layers adjacent to the matrix.
 - Peroxides are use for dynamic vulcanization and the blend is transformed into a thermoplastic vulcanizate. A mixture of peroxides is used. Trigonox 311, which is designed to work at high temperatures and DCP, which is standard peroxide used for TPV's, were used synergetic effects and compare processing and physical properties of the composites. The composition consisting on 40% HDPE 30% EPDM 30% GTR 0.5% Trigonox 311 and 0.1% DCP gives the best TPV mechanical properties.
- The maximum amount of GTR particles in the final blend was desired in order to help the global reduction of EOL tyres. The blend consisting on 40% HDPE 30% EPDM 30% GTR 0.5% Trigonox 311 and 0.1% DCP gives the best balance regarding GTR amount (30%) and mechanical properties without deleterious defects.
- Due to cost savings, it was a premise to have a compatibilization method that does not need many complications to be applied (e.g. especial machines, etc...). Besides the acid treatment, which need an step more in order to apply the pre-treatment onto the GTR particles, the rest of the methods do not need any special handling or special equipment as the raw materials used can be add directly to the mixture.

4. Acknowledgment

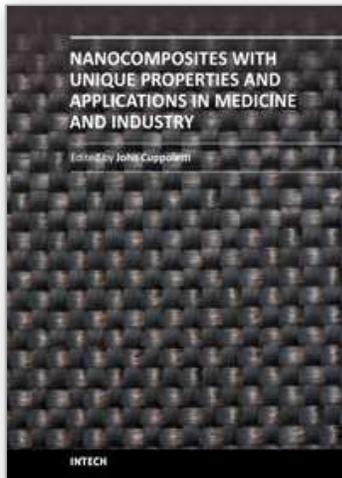
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This book contains chapters on nanocomposites for engineering hard materials for high performance aircraft, rocket and automobile use, using laser pulses to form metal coatings on glass and quartz, and also tungsten carbide-cobalt nanoparticles using high voltage discharges. A major section of this book is largely devoted to chapters outlining and applying analytic methods needed for studies of nanocomposites. As such, this book will serve as good resource for such analytic methods.

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